SCIENCE FOR CERAMIC PRODUCTION

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PROMISING ARGILLACEOUS MATERIALS FOR FINE AND STRUCTURAL CERAMICS

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The results of studying the composition, structure, and properties of Kailinskoe clay are considered. The possibility for producing ceramic materials with a light-colored crock based on mineral material from the Siberian region is demonstrated.

In terms of the current demand for domestic consumer goods and the need to save high-quality resources and transport expenses, it is essential to develop new material deposits, to complete the exploration of the earlier prospected deposits, and to involve them in the production of various ceramics.

The Kailinskoe deposit of mineral materials (quartz sands and clays) is situated near Andzhero-Sudzhensk (Kemerovo Region). This argillaceous material is a homogeneous rock of light gray (almost white) color and dense structure, virtually without extraneous inclusions. The prospected reserves of this clay are predominantly in the category C_1. The overall reserves in the categories $A + B + C_1$ are substantial and amount to 1400 thousand tons [1]. Moreover, the Kailinskoe sands contain argillaceous impurities (their content reaches 20 – 25%) removed by elutriation.

As the ceramic industry in Russia is currently experiencing a shortage of high-quality clay materials, it is interesting to compare the properties of the considered material with the properties of the Veselovskoe clay (Ukraine) and the Troshkovskoe clay (Russia), which are of high quality and widely used in various ceramic technologies.

The results of the evaluation of the granulometric composition of the considered material obtained by the sedimentation method according to GOST 2126.1–81 are given in Table 1; in accordance with GOST 9169–75 this material is classified as a medium-disperse material whose content of particles < 0.001 mm is below 60%, and according to the Okhotin diagram, it is classified as plastic clay.

Based on its chemical composition (Table 2), depending on the content of Al_2O_3 and Fe_2O_3, Kailinskoe clay in the calcined state is assigned to the semi-acid group (21.43% Al_2O_3) with a medium content of coloring oxides (2.25% Fe_2O_3).

The results of an integrated study of the qualitative mineralogical composition of Kailinskoe clay reveal its predominantly kaolinite composition with a certain impurity of hydromica, which is indicated by the presence of the basal x-ray reflections in the diffraction patterns at 0.721 (001) and 0.357 (002) nm in the case of kaolinite and at 1.003 (001) and 0.445 (110) nm in the case of hydromica (Fig. 1), as well as the clearly expressed effects at temperatures of 560 and 980°C on the DTA curve (Fig. 2) and the principal mass loss (over 60%) registered within the temperature range of 500 – 1000°C on the thermogram curve, determined by dehydration of kaolinite. Moreover, the main clay-forming mineral (kaolinite) is characterized by a low degree of structural ordering, which is indicated by the absence of x-ray reflections patterns within the interplanar distance interval of 0.25

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TABLE 1

Clay	Particles content, %, of size, mm					Classification by GOST 9169–75
	1 – 0.06	0.06 – 0.01	0.01 – 0.005	0.005 – 0.001	< 0.001	
Kailinskoe	8.66	5.25	9.86	25.74	50.47	Medium-disperse
Veselovskoe	3.87	6.03	9.79	21.26	56.06	The same
Troshkovskoe	6.38	12.31	5.43	11.88	66.00	High-disperse

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TABLE 2

Clay	Mass content, %							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	calcination loss
Kailinskoe	64.33	19.27	2.02	1.43	1.54	0.51	0.91	9.90
Veselovskoe	55.93	27.97	0.93	1.77	–	0.51	1.65	10.50
Troshkovskoe	55.51	30.48	1.17	1.68	1.87	0.15	0.25	8.89

TABLE 3

Mineral	Content, %	Characteristics
Kaolinite	37.8	Argillaceous, containing the fraction below 5 μm
Hydromica	14.4	The same
Free quartz	37.1	Mostly in the form of fine-disperse fraction
Feldspar	4.4	In the form of albite, in the coarse-grained part
Calcite	2.6	In the coarse-grained state
Magnesite	2.3	The same
Ferrous	1.4	In the fine-disperse state

– 0.35 nm on the diffraction patterns, whereas the kaolinites with a perfect crystalline structure exhibit four clear reflections within the specified interval [2]. The quantitative estimate of the crystallinity index using the Hinckley ordering method represented by the ratio of intensities of x-ray reflections (110) and (111) [3], which was equal to 0.3, is another evidence of the disorder (defectiveness) of the kaolinite structure in the considered clays.

Based on the chemical analysis data and the established qualitative mineralogical composition of Kailinskoe clay, the quantitative mineralogical composition of the studied sample was calculated (Table 3).

The specifics of the granulometric composition (a high content of finely disperse particles), mineralogical composition (the presence of hydromica), as well as the structure of the main clay-forming mineral (kaolinite disorder) have a positive effect on several technological properties and provide sufficient plasticity (plasticity number equal to 16), coherence and binding capacity (it binds 60% sand), low drying sensitivity (0.65), and refractoriness (Table 4, Fig. 3).

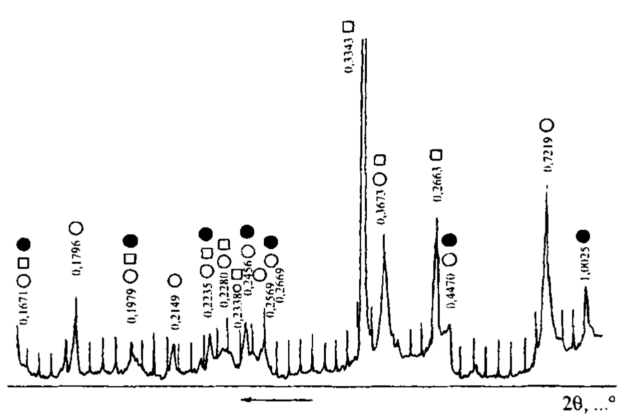

Fig. 1. Diffraction pattern of Kailinskoe clay: O) kaolinite; □) quartz; ●) hydromica.

TABLE 4

Parameter	Clay		
	Kailinskoe	Veselovskoe	Troshkovskoe
Al_2O_3 content in calcined state, %	21.41	31.24	33.31
Plasticity number	16	20	24*
Coherence (compressive strength), MPa	4.3	4.2	5.6*
Binding capacity (% chamotte)	60	80	60*
Drying sensitivity	0.65	0.75	0.66
Air shrinkage, %	6.0	8.3	8.4
Temperature of, °C:			
beginning of sintering	1150	1100	1100
complete sintering	1400	1300	1400
Refractoriness, °C**	1650	1680	1700
Crock color	Light yellow	White	

* After machine treatment.
** Estimated.

Thus, Kailinskoe clay in a number of its main technological properties is not inferior to high-quality Veselovskoe and Troshkovskoe clays, especially in its plastic and molding properties, which is significant when it is used as the binding component in semidry production technologies, but is slightly inferior in refractoriness.

The physicochemical and technological specifics of the considered clay point to the expedience of its testing in ceramic compositions with light-colored crock, for example, majolica and facing tiles.

The traditional notions of the compositions of fine ceramic mixtures have significantly changed of late, and these mixtures are currently produced using non-traditional non-plastic materials. For example, the flux is represented not by hard-to-get feldspar-bearing rocks, but by various-purpose

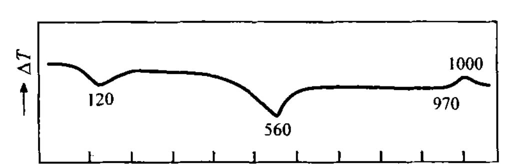

Fig. 2. DTA curve of Kailinskoe clay.

glass cullet, and the grog component is represented by calcium-magnesium-silicate material. Moreover, the faience and majolica mixtures have a higher fraction (than porcelain mixtures) of the plastic component (clays and kaolins) which attains 75 – 85% and higher.

In this context, the experimental majolica and tile mixtures were prepared using the typical quartz-bearing component (Tuganskii sand from Tomsk and Andzhero-Sudzhenskii quartzite), as well as calcium-magnesium-silicate Siberian rocks which had earlier proved successful [4, 5], i.e., diopside-quartz rock (82 – 85% diopside, 13 – 15% quartz) from the Slyudyanskoe deposit and tremolite-calcite rock (61 – 63% tremolite, 37 – 40% calcite) from the Alguiskoe deposit. For the low-melting component, such efficient fluxes as electric bulb cullet S-92 and Vyshnevogorskii nepheline sienite (for tile mixtures) were tested as the low-melting component.

The mixture were prepared by joint wet fine grinding of raw materials in a ball mill. The compositions of the majolica mixtures are given in Table 5.

Since majolica articles were molded by casting into gypsum molds, special attention was paid to the assessment (using the standard methods) and adjustment of the rheological properties of the slip mixtures.

The necessary fluidity of the suspension was provided by the introduction of liquefiers such as soda and liquid glass in amounts of 0.3 and 0.1%, respectively.

It was found that the slips of all considered compositions exhibit increased moisture (40 – 47%); as for the other monitored parameters (fluidity, i.e., efflux time in the Engler viscosimeter — from 9 to 18 sec, thickening — from 1.7 to 2.4, stratification resistance according to Gribovskii — 200), they meet the requirements imposed on the properties of majolica (faience) casting slips.

Visual observation of the slip behavior in casting and the behavior of the cast sample in drying indicate that the crock formation in all slips proceeds without complication, i.e., the use of the Kailinskoe clay plastic ingredient in the amount of 60 – 70% is sufficient for molding articles by the slip casting method.

The intermediate product dried to the air-dry state was fired in a Silit furnace at a rate of 3 – 4°C/min at temperatures of 950, 1000, and 1050°C and holding at the end temperature for 0.5 h.

A comparative analysis of ceramic properties of the considered mixtures indicates that the most promising in practical terms are the quartz-bearing mixtures with 35% grog addition (mixtures M3, M4) fired at the temperature of 1050°C, since they have relatively low overall shrinkage (7.1 and 9.4%), a required level of water absorption (9.5 and 9.7%), and sufficiently high compressive strength (31.5 and 31.9 MPa). Mixtures M1, M2, and M5 fired at the same temperature, although exhibiting high strength (50, 56, and 34 MPa, respectively), show considerable total shrinkage (11.6 – 12.0%), which makes it difficult to ensure size and shape precision of the products in drying and firing.

TABLE 5

Mixture	Mass content, %				
	clay	sand	quartzite	diopside	cullet
M1	70	15	–	–	15
M2	60	20	–	–	20
M3	65	25	–	–	10
M4	65	–	25	–	10
M5	65	–	–	25	10

Moreover, analysis of the effect of the qualitative composition of the grog additives demonstrated that replacement of the imported diopside material (mixture M5) by the less expensive and more available quartz material (sands and quartzites) in the equivalent ratio (mixtures M3 and M4) has virtually no effect on the crock characteristics and makes it possible to obtain highly artistic thin-walled products based exclusively on the local raw materials by low-temperature firing.

The testing of Kailinskoe clay in ceramic facing tile mixtures was carried out taking into account standard compositions in which the proportion of the clay materials should be at the level of 48 – 52%. The ratio between the argillaceous, grog, and flux components was selected so that the firing shrinkage of the mixture would not exceed 2%. Therefore, for the purpose of decreasing the shrinkage and strengthening the finished article, diopside and tremolite rocks were used in the grog component along with the traditionally used quartzite, quartz sand, and chamotte of the tested clay (Table 6).

The mixture was prepared in accordance with the slip technology by joint fine grinding up to a residue below 10% on a No. 0063 sieve. The resulting slips with 45 – 48% moisture had sufficient fluidity (16 sec in the Engler viscosimeter) and low thickening (1.4 – 1.6).

Molding powders were prepared by drying the slips with their subsequent grinding, classification, and preparation of

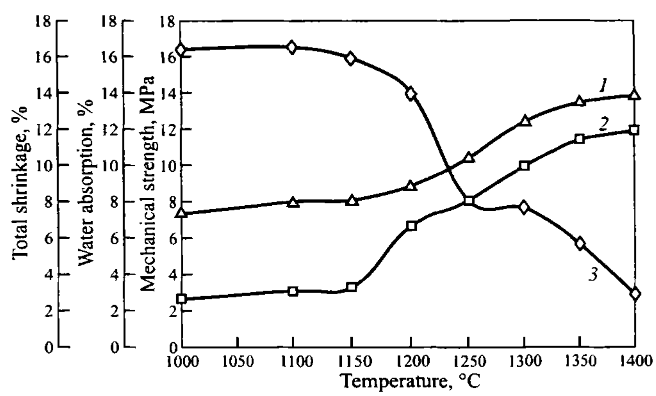

Fig. 3. Dependence of the linear dimensions (*1*), mechanical strength (*1*), and water absorption of Kailinskoe clay on firing temperature.

TABLE 6

Raw material	Mixture				
	P1	P2	P3	P4	P5
Kailinskoe clay	70	60	60	50	50
Tuganskii sand	–	–	–	20	–
Antonovskoe quartzite	15	25	–	–	–
Chamotte (of the Kailinskoe clay)	–	–	–	10	–
Diopside rock	–	–	30	–	–
Tremolite rock	–	–	–	–	30
Nepheline sienite	–	–	–	20	–
Cullet	15	15	10	–	20

the powder with the standard granular composition and moisture (6.8 – 7.5%).

The articles were molded by compression at the deliberately selected pressure (15 – 16 MPa) providing for the required bending strength of raw material (over 0.6 MPa).

The articles were fired in electric furnaces with Silit heaters at temperatures from 980 to 1100°C with holding for 0.5 h at the end temperature.

Comparative analysis of the results reveals that the required water absorption (10.6, 15.2, and 10.3%) of the articles made of mixtures P1, P2, and P3 in which cullet is the only flux is attained at the temperature of 980 – 1000°C. However, they exhibit inadmissibly high shrinkage (6.0 – 7.3%). An increase in the firing temperature of these mixtures up to 1000 – 1020°C helps to decrease the shrinkage to 3.2 – 4.3% with a simultaneous increase in porosity due to the polymorphic transformations of quartz introduced into these mixtures in quartzites (mixtures P1 and P2) and diopside-quartz rock (mixture P3). A further increase in the firing temperature of the quartz-containing mixtures (P1, P2) is again accompanied by an increase in their shrinkage (up to 5.9 – 6.7%) due to the intensification of the sintering process. Heat treatment of the diopside mixture P3 at temperatures of 1040 – 1060°C yields products whose properties meet the imposed requirements (shrinkage 2.2%, water absorption 14.9%, bending strength 35.3 MPa). This is determined by the specifics of phase formation in diopside-containing mixtures, in particular, the formation of anorthite at the temperature of 1000 – 1100°C, which refines the tile properties.

A decrease in the fraction of the plastic component (the Kailinskoe clay) from 70 to 50% (mixtures P4 and P5) and the use of nepheline sienite as a flux in the composition of mixture P4 make it possible to attain the required water absorption (15.1%) and sufficiently high bending strength (36 MPa) at the temperature of 1020 – 1040°C. The firing shrinkage in this case does not exceed 3.0%, which, as in the case of the diopside-containing mixture P3, makes this mixture promising for industrial use.

The use of tremolite-containing rock in the nonplastic part of mixture P5 (up to 30%) made it possible to produce articles whose strength significantly exceeds the standard requirements (over 40 MPa) and prescribed shrinkage. However, the specifics of the mineralogical composition of the specified grog additive (calcite content up to 35 – 40%) makes it necessary to raise the firing temperature to 1080 – 1100°C to attain the required degree of sintering (water absorption not more than 16%).

Thus, the development of refractory clays from the Kailinskoe deposit and the use of tremolite and diopside rocks will contribute to solving the problem of domestic material resources and provide for production of various ceramics with light-colored crock in the eastern regions of Russia using local raw materials.

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